Kinetic Resolution of Planar-Chiral (η^5-Bromocyclopentadienyl)manganese(I) Complexes by Molybdenum-Catalyzed Asymmetric Ring-Closing Metathesis

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Supporting Information Placeholder

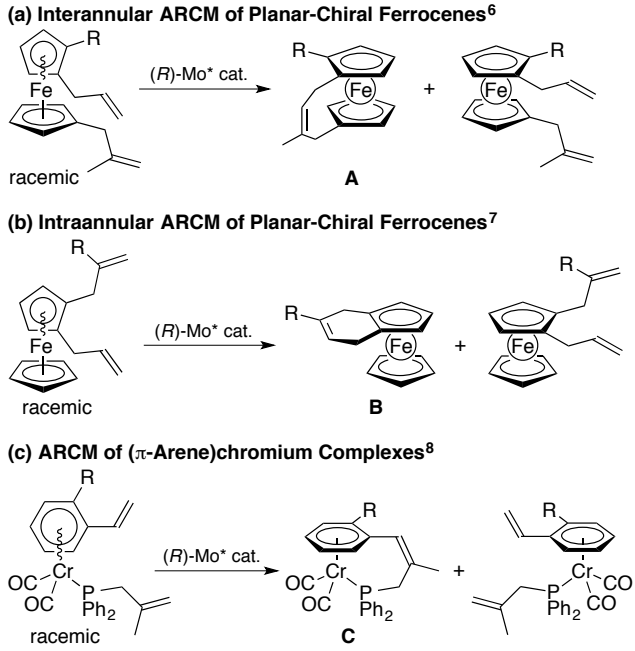
ABSTRACT: Kinetic resolution of racemic planar-chiral (η^5-1-alkenyl-2-bromocyclopentadienyl)manganese(I) complexes **1** was realized by the molybdenum-catalyzed asymmetric ring-closing metathesis. While vinyl-Cp derivative **1a** was resolved in excellent enantioselectivity with the k_{rel} values of up to 127, the selectivity in the ARCM reaction of allyl-Cp derivative **1b** was modest (k_{rel} = 3.0). ARCM product **2a**, which was obtained in an enantiomerically pure form by the two successive ARCM reactions or recrystallization of the enantiomerically enriched products, was found to be a versatile synthetic precursor to various planar-chiral cymantrene derivatives.

INTRODUCTION

Cymantrene, (η^5-cyclopentadienyl)manganese(I) tricarbonyl, and its derivatives are one of the most well-studied half-sandwich complexes in organometallic chemistry.[1] Steric modification of the parent cymantrene can be attained by the two ways; one is substitution at the η^5-cyclopentadienyl hydrogens, and the other is replacement of the carbonyl ligands with appropriate two-electron donors. When more than one "different" substituents are introduced in the η^5-cyclopentadienide in an unsymmetrical fashion, the symmetry of cymantrene is broken and so-called planar chirality is induced in the compound.[2] Analogous planar chirality is frequently seen in substituted ferrocenes, zirconocenes, and (π-arene)chromium(0) complexes as well.[3] Planar-chiral transition-metal complexes are important chiral scaffolds in organic/organometallic chemistry, however, their preparative methods in optically active forms are rather limited. And indeed, *catalytic asymmetric synthesis* of such planar-chiral species has been extremely rare.[3e,4,6-8]

Recently, we disclosed that the asymmetric ring-closing metathesis (ARCM)[5] of 1,1'-diallylferrocene substrates was highly effective to control ferrocene-based planar chirality affording the corresponding bridged ferrocenes **A** of high enantiomeric purity (interannular RCM; Scheme 1, (a)).[6] The ARCM protocol was applied to the reaction of 1,2-diallylferrocene derivatives (intraannular RCM; Scheme 1, (b)) as well, and various non-bridged planar-chiral ferrocenes **B** were obtained with enantiomeric enrichment.[7] Asymmetric synthesis of planar-chiral (π-arene)chromium complexes was also achieved by the analogous ARCM reactions of (η^6-alkenylarene)(alkenylphosphine)chromium(0) dicarbonyl complexes (Scheme 1, (c)).[8]

Scheme 1. Reported Systems for Kinetic Resolution of Planar-Chiral Complexes by Asymmetric Ring-Closing Metathesis



In this article, we have examined an extension of the ARCM method to the kinetic resolution of racemic planar-chiral cymantrene derivatives. The substrates employed in this study are *rac*-[η^5-1-(ω-alkenyl)-2-bromocyclopentadienyl](diphenylmethallylphosphine)manganese(I) dicarbonyl complexes (*rac*-**1**).[9] The structural motifs in RCM products **2** can be regarded as a hybrid of those in ferrocenes **A** and (π-arene)chromium complexes **C**, whose

ARCM preparations were reported previously.[6,8] The "bromo"-cyclopentadienide moieties in **2** can be easily converted to various functional groups by standard organic transformations with retention of the planar-chirality, and thus the planar-chiral manganese complexes prepared in this report are considered as versatile precursors to various planar-chiral cymantrene derivatives. Indeed, we demonstrated recently that the diarylphosphino-derivatives prepared from (*R*)- or (*S*)-**2a** were outstanding chiral phosphine-olefin ligands in the various rhodium-catalyzed asymmetric reactions.[10] It should be noted that, to the best of our knowledge, this work is the first example of *catalytic* asymmetric synthesis of planar-chiral CpMn(I) half-sandwich complexes.[2]

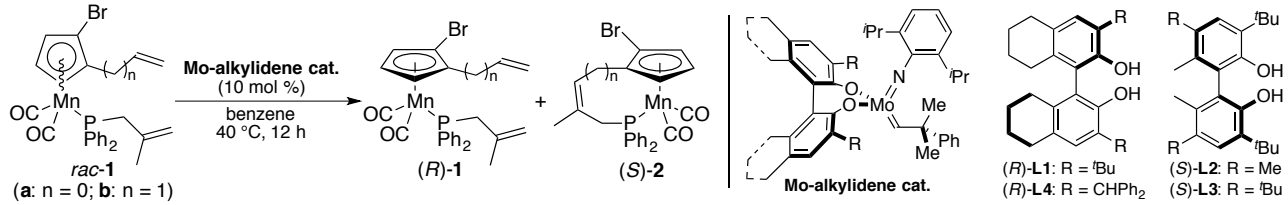
RESULTS AND DISCUSSION

Kinetic Resolution of Racemic Planar-Chiral Cymantrene Derivatives 1 by Molybdenum-Catalyzed Asymmetric Ring-Closing Metathesis (ARCM). The substrates used in this study are (η^5-1-bromo-2-ω-alkenylcyclopentadienyl)(methallyldiphenylphosphine)manganese(I) dicarbonyl, where the "ω-alkenyl" substituent in the η^5-cyclopentadienide is vinyl (**1a**) or allyl (**1b**) groups.[9] While the ω-alkenyl group in **1** is monosubstituted olefin, the methallyl group in the coordinating phosphine is disubstituted one. This would effectively discriminate the two olefinic reaction sites in **1** leading to the better enantioselectivity in the ARCM.[6-8]

At the outset, screening of chiral molybdenum-alkylidene precatalysts was examined using *rac*-**1a** as a prototypical substrate. The asymmetric reactions were carried out in benzene at 40 °C in the presence of an appropriate chiral Mo-precatalyst (10 mol %), that was generated in situ from the Mo-precursor, (pyrrolyl)$_2$Mo(=CHCMe$_2$Ph)(=N-C$_6$H$_3$-2,6-^{i}Pr$_2$), and an axially chiral biphenol derivative (Table 1).[11] Under these conditions, the Mo-precatalyst generated with (*R*)-**L1**[12a] gave RCM product **2a** of 81% ee in 49% yield, and unreacted **1a** of 89% ee was recovered in 46% yield (Table 1, entry 1). The k_{rel} value ([reaction rate of the fast-reacting enantiomer]/[reaction rate of the slow-reacting enantiomer]; selectivity factor) for this reaction was estimated to be 28.[13] It was found that the Mo-precatalyst coordinated with (*S*)-**L2**[12b] showed excellent enantioselectivity giving **2a** of 93% ee in 50% yield and **1a** of 98% ee in 47% yield. The k_{rel} value for the reaction is as high as 127, and the nearly perfect kinetic resolution of two enantiomers in *rac*-**1a** was achieved (entry 2). With the lower catalyst loading (5 mol %) of Mo/(*S*)-**L2**, the reaction was slower with less than 50% conversion in 12 h, however, the selectivity was still excellent (k_{rel} = 84; entry 3). The Mo precatalyst prepared with (*S*)-**L3**[12c] also showed excellent performance, but the selectivity was slightly inferior to that of Mo/(*S*)-**L2** (entry 4). The Mo/(*R*)-**L4** species[12d] was too active for the ring-closing metathesis of **1a**; the reaction of *rac*-**1a** using this precatalyst showed complete conversion to *rac*-**2a** under the conditions examined and no effective kinetic resolution was observed (entry 5).

The two best ligands for the kinetic resolution of *rac*-**1a**, namely (*S*)-**L2** and (*S*)-**L3**, were applied to the molybdenum-catalyzed ARCM reaction of *rac*-**1b**. However, the kinetic resolution of *rac*-**1b** was much less effective and the k_{rel} values were 3.0 at most (entries 6 and 7). The enantioselectivity in the kinetic resolution of *rac*-**1** was sensitive to the lengths of the ω-alkenyl substituents in the η^5-cyclopentadienides. The similar trend was observed in the ARCM kinetic resolution of (η^6-alkenylarene)(alkenylphosphine)Cr(0) dicarbonyl substrates; while the (η^6-styrene)Cr(0) derivatives showed excellent selectivity in the ARCM kinetic resolution with the k_{rel} values of up to 198, the (η^6-allylbenzene)Cr(0) species was an improper substrate showing very poor selectivity (k_{rel} = 3.0).[8a]

Table 1. Molybdenum-Catalyzed ARCM Kinetic Resolution of Racemic Planar-Chiral (η^5-Cyclopentadienyl)Mn(I) Complexes 1[a]



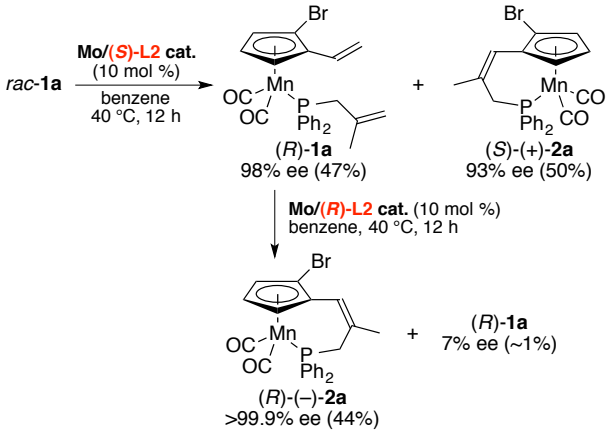
entry	substrate	chiral **L**	recovered **1**		cyclized **2**		config./optical rotation sign of **2**	calculated conv. (%)[e]	k_{rel}[e]
			%ee[b,c]	yield (%)[d]	%ee[c]	yield (%)[d]			
1	**1a**	(*R*)-**L1**	89	46	81	49	(*R*)-(–)	52	28
2	**1a**	(*S*)-**L2**	98	47	93	50	(*S*)-(+)	51	127
3[f]	**1a**	(*S*)-**L2**	72	52	95	45	(*S*)-(+)	43	84
4	**1a**	(*S*)-**L3**	97	45	88	50	(*S*)-(+)	52	65
5	**1a**	(*R*)-**L4**	----[g]	<1	<1	98	----[g]	>99	----[g]
6	**1b**	(*S*)-**L2**	35	48	37	45	(+)	49	3.0
7	**1b**	(*S*)-**L3**	25	50	29	39	(+)	46	2.3

[a] The reaction was carried out in benzene in the presence of an appropriate metathesis catalyst generated in situ (10 mol %) unless otherwise noted. [b] Determined after conversion into **2** by a reaction with the Grubbs-II catalyst. [c] Determined by chiral HPLC (see Supporting Information for detail). [d] Isolated yield by preparative GPC. [e] Calculated based on a first-order equation (ref. 13). [f] With 5 mol % catalyst loading. [g] Not determined.

By the combination of the two successive ARCM kinetic resolution of *rac*-**1a**, (*R*)-(–)-**2a** could be obtained in a practically enantiomerically pure form. After the first kinetic resolution of *rac*-**1a** catalyzed by Mo/(*S*)-**L2** as in Table 1, the recovered substrate,

(*R*)-**1a** of 98% ee, was subjected to the second ARCM kinetic resolution using the antipodal molybdenum-alkylidene precatalyst, Mo/(*R*)-**L2**, to give (*R*)-(−)-**2a** in >99.9% ee (Scheme 2).

Scheme 2. Two Successive ARCM Kinetic Resolution of *rac*-1a Giving Enantiomerically Pure (*R*)-(−)-2a



Determination of Absolute Configuration of (−)-2a. Single crystals of levorotatory **2a** ($[\alpha]^{22}_{D}$ −135 (*c* 0.35 in EtOAc)) suitable for X-ray crystallography were grown as yellow-orange prisms by slow diffusion of pentane into the concentrated dichloromethane solution of (−)-**2a**, and the crystallography revealed its three-dimensional structure of which absolute configuration to be (*R*). The unit cell contains three independent molecules, having slightly different conformations, and the structure of one of the three crystallographically independent molecules is shown in Figure 1 with selected atom labels (see Supporting Information for details).

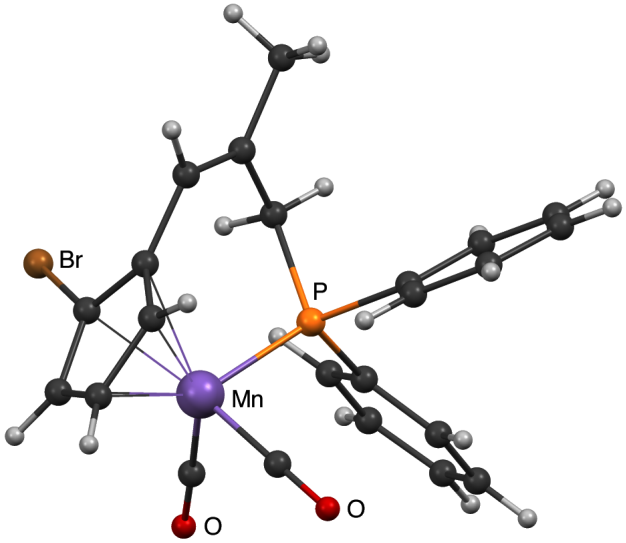
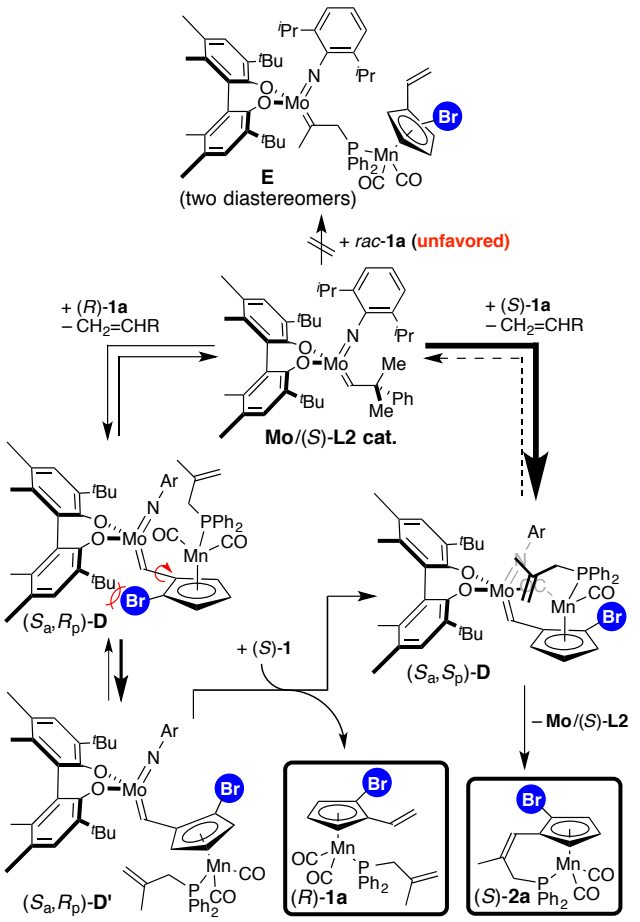


Figure 1. Ball-and-stick drawing of (*R*)-(−)-**2a** with selected atom labels.

Consideration of Stereochemical Pathways of Molybdenum-Catalyzed ARCM Kinetic Resolution of 1. Plausible reaction pathways of the Mo-catalyzed ARCM kinetic resolution of *rac*-**1a** are illustrated in Scheme 3. Whereas a less substituted olefin is more reactive than a more substituted one in olefin metathesis, the initial reaction between Mo/(*S*)-**L2** and (*S*)- or (*R*)-**1a** might take place at the Cp-bound vinyl group to form a pair of diastereomeric intermediates (S_a,S_p)-**D** or (S_a,R_p)-**D**, and the formation of intermediate **E** is unlikely. The phosphorus-bound methallylic olefin in (S_a,S_p)-**D** is able to take a position proximal to the molybdenum center, and thus (S_a,S_p)-**D** provides bridged product (*S*)-**2a** smoothly by the intramolecular second metathesis. On the other hand, epimeric (S_a,R_p)-**D** is forced to take non-productive conformation in (S_a,R_p)-**D'** due to the steric repulsion between the Cp-bound bromo-substituent and the *tert*-butyl group in the chiral biaryloxide ligand. Subsequent intermolecular metathesis between (S_a,R_p)-**D'** and (*S*)-**1a** liberates (*R*)-**1a** intact together with productive intermediate (S_a,S_p)-**D**.

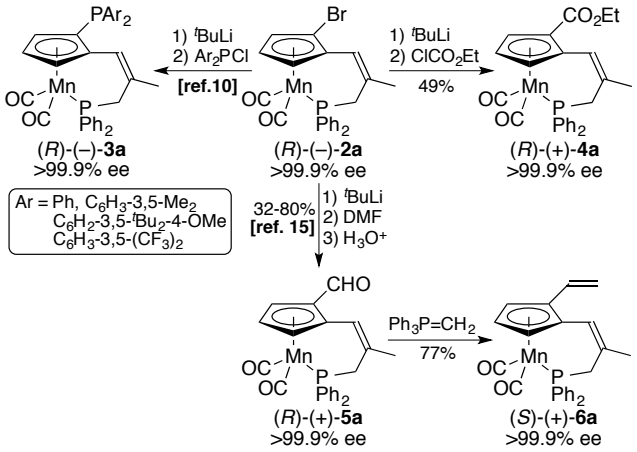
Scheme 3. Plausible Stereochemical Pathways of ARCM Kinetic Resolution of *rac*-1a Catalyzed by Mo/(*S*)-L2



Derivatizing Single-Enantiomeric (*R*)-(−)-2a. Enantiomerically pure (*R*)-(−)-**2a** was prepared as above (Scheme 3). Alternatively, single-enantiomeric (*R*)- or (*S*)-**2a** was obtained by recrystallization of the enantiomerically enriched samples prepared by the Mo-catalyzed ARCM shown in Table 1. The bromo substituent in **2a** can be lithiated under the standard conditions, and the subsequent reactions with an appropriate electrophile give the corresponding planar-chiral cymantrene derivatives in good yields with complete retention of the optical purity in **2a** (Scheme 4). Recently, we demonstrated that a series of planar-chiral phosphine-olefin ligands **3a**, which showed outstanding performances in the various rhodium-catalyzed asymmetric carbon-carbon bond formation reactions, were prepared from (*R*)- or (*S*)-**2a**.[10] Single-enantiomeric ethoxycarbonyl derivative (*R*)-(+)-**4a** was obtained by the reaction of the generated lithio-species with ethyl chloroformate in 49% yield starting with (*R*)-(−)-**2a**. In the same way, a formyl group can be introduced in (*R*)-(+)-**5a** by the reaction with

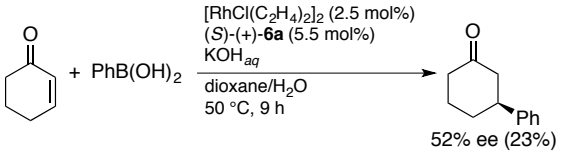
DMF.[14,15] Subsequent Wittig methylenation of the formyl group in (*R*)-**5a** provided vinyl-substituted (*S*)-(+)-**6a** in 77% yield in an enantiomerically pure form.

Scheme 4. Enantioretentive Conversion of (*R*)-(–)-2a into Various Planar-Chiral (η⁵-Cyclopentadienyl)manganese(I) Complexes



During the last decade, several conceptually novel chiral dienes have been elaborated and have demonstrated to be useful chiral ligands in various rhodium- and iridium-catalyzed asymmetric reactions.[16] In light of the structural similarity between (*S*)-**6a** and (*R*)-**3a**, the latter was shown to be an exceptional chiral phosphine-olefin ligand in the various rhodium(I)-catalyzed reactions,[10] the synthetic utility of (*S*)-**6a** as a chiral diene ligand is examined in the rhodium(I)-catalyzed asymmetric 1,4-addition of phenylboronic acid to 2-cyclohexenone (Scheme 5).[17] Although the enantioselectivity and the catalytic activity of the Rh/(*S*)-**6a** species are rather insufficient and need further improvement, the result shown in Scheme 5 clearly indicates the potential validity of (*S*)-**6a** as a chiral ligand in transition-metal catalysis.

Scheme 5. Asymmetric 1,4-Addition of Phenylboronic Acid to 2-Cyclohexenone Catalyzed by Rhodium/(*S*)-(+)-6a



CONCLUSIONS

In summary, we have developed a method for the kinetic resolution of racemic planar-chiral (η⁵-1-alkenyl-2-bromocyclopentadienyl)manganese(I) complexes by the molybdenum-catalyzed asymmetric ring-closing metathesis. While vinyl-Cp derivative **1a** was resolved in excellent enantioselectivity with the k_{rel} values of up to 127, the selectivity in the ARCM reaction of allyl-Cp derivative **1b** was modest (k_{rel} = 3.0). ARCM product **2a**, which was obtained in an enantiomerically pure form by the two successive ARCM reactions or recrystallization of the enantiomerically enriched products, could serve for the versatile synthetic precursor and was converted to various planar-chiral cymantrene derivatives with retention of the enantiomeric homogeneity. This study, together with our previous reports,[6-8] reveals that the molybdenum-catalyzed asymmetric metathesis reaction is a powerful tool to control peripheral chirality in various transition-metal complexes.

EXPERIMENTAL SECTION

General Information. All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 100 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P NMR (at 162 MHz) chemical shifts are externally referenced to 85% H_3PO_4. Tetrahydrofuran and benzene were distilled from benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. Racemic substrates (**1a** and **1b**),[9] (pyrrolyl)$_2$Mo(=CHCMe$_2$Ph)(=N-C$_6$H$_3$-2,6-^{i}Pr$_2$),[11] (*R*)-**L1**,[12a] (*S*)-**L3**,[12c] (*R*)-**L4**,[12d] and the Grubbs-II catalyst[18] were prepared according to the reported methods. All the other chemicals were obtained from commercial sources and used as received unless otherwise noted.

General Procedure for Molybdenum-Catalyzed ARCM Kinetic Resolution of *rac*-1. In a glovebox under prepurified argon, Mo(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(=CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$ (1.5 mg, 2.9 μmol) and an appropriate chiral ligand **L** (2.9 μmol) were dissolved in dry benzene (1.5 mL) in a test tube with a Teflon-sealed screw cap. After stirring the mixture for 15 min at room temperature, to this were added benzene (3 mL) and substrate **1** (29 μmol). The test tube was sealed tightly and taken out of the glovebox. The test tube was immersed in an oil bath maintained at 40 °C and the mixture was stirred for 12 h. After quenching the reaction by addition of acetone (ca. 100 μL), the reaction mixture was passed through a short pad of silica gel using hexane/Et$_2$O (9/1) as an eluent. The solvent was removed under reduced pressure, and the residue was purified by preparative HPLC [LC-908 recycle HPLC system (Japan Analytical Industry Co. Ltd.) with a GPC column (JAIGEL-H, chloroform, 3.5 mL/min)] to give the ARCM product **2** and the recovered substrate **1**. Recovered **1** was converted to the corresponding **2** by the reaction with the Grubbs-II catalyst (5 mol %) in benzene for a chiral HPLC analysis. The characterization data of the ARCM products and the conditions for the chiral HPLC analysis are described below.

(*R*)-(–)-[(η⁵-1-Bromo-2-(3-diphenylphosphino-2-methylpropenyl)cyclopentadienyl-*P*)]manganese(I) Dicarbonyl ((*R*)-(–)-2a). The racemate of this compound was reported and fully characterized in our previous report.[9] [α]$^{22}_D$ = –135 (*c* 0.35, EtOAc). Chiral HPLC Analysis Conditions: Daicel Chiralcel OD-H; eluent, hexane/^{i}PrOH = 100/1; flow rate, 0.8 mL/min; t_1 = 12.2 min [(*S*)-(+)-isomer], t_2 = 19.7 min [(*R*)-(–)-isomer].

(+)-[(η⁵-1-Bromo-2-(4-diphenylphosphino-3-methylbutenyl)cyclopentadienyl-*P*)]manganese(I) Dicarbonyl ((+)-2b). The racemate of this compound was reported and fully characterized in our previous report.[9] [α]$^{25}_D$ = +12.2 (*c* 0.17, CHCl$_3$ for the sample of 37% ee). Chiral HPLC Analysis Conditions: Daicel Chiralpak AD-H; eluent, hexane/^{i}PrOH = 25/1; flow rate, 0.8 mL/min; t_1 = 7.2 min [(–)-isomer], t_2 = 8.7 min [(+)-isomer].

(*R*)-(+)-[(η⁵-1-(3-Diphenylphosphino-2-methylpropenyl)-cyclopentadienyl-2-ethoxycarbonyl-*P*)]manganese(I) Dicarbonyl (4a). To a solution of (*R*)-(–)-**2a** (99 mg, 0.20 mmol) in THF (3 mL) was added ^{t}BuLi (1.64 M in pentane, 0.27 mL, 0.44 mmol) dropwise at –78 °C. After stirring the solution for 1 h at –

78 °C, ethyl chloroformate (33 mg, 0.30 mmol) was added dropwise, then the resulting mixture was gradually warmed to room temperature. The mixture was quenched with saturated NH_4Cl_{aq}, and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and filtered. The filtered was concentrated on a rotary evaporator. The crude mixture was purified by silica gel column chromatography to give the product as a yellow solid (47.4 mg, 49%). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, *J* = 7.3 Hz, 3H), 1.62 (s, 3H), 2.85 (dd, *J* = 13.3 and 7.3 Hz, 1H), 3.16 (t, *J* = 13.3 Hz, 1H), 4.04-4.12 (m, 1H), 4.15 (s, 1H), 4.24-4.32 (m, 1H), 4.86 (t, *J* = 2.7 Hz, 1H), 5.21-5.22 (m, 1H), 6.21 (br, 1H), 7.33-7.42 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.3 (s), 27.1 (s), 34.0 (d, J_{PC} = 19.4 Hz), 60.3 (s), 79.2 (s), 81.4 (s), 81.6 (s), 83.3 (s), 102.9 (s), 117.6 (d, J_{PC} = 11.1 Hz), 128.0 (d, J_{PC} = 9.4 Hz), 128.2 (d, J_{PC} = 8.3 Hz), 129.5 (s), 129.8 (s), 131.1 (d, J_{PC} = 8.6 Hz), 132.1 (d, J_{PC} = 9.4 Hz), 136.1 (d, J_{PC} = 38.1 Hz), 136.2 (s), 138.7 (d, J_{PC} = 42.3 Hz), 167.1 (s), 229.3 (d, J_{PC} = 24.3 Hz), 229.9 (d, J_{PC} = 26.0 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ (s). ES-HRMS Calcd for $C_{26}H_{24}MnNaO_4P$ (M+Na): 509.0690. Found: 509.0667. $[\alpha]_D^{24}$ +130 (*c* 0.16, EtOAc for the sample of >99.9% ee).

(*R*)-(+)-[(η^5-1-(3-Diphenylphosphino-2-methylpropenyl)-cyclopentadienyl-2-formyl-*P*)]manganese(I) Dicarbonyl (5a). To a solution of (*R*)-(−)-**2a** (150 mg, 0.304 mmol) in THF (10 mL) was added ^{t}BuLi (1.64 M in pentane, 0.40 mL, 0.656 mmol) dropwise at −78 °C. After stirring the solution for 1 h at −78 °C, DMF (51 mg, 0.70 mmol) was added dropwise, then the resulting mixture was gradually warmed to room temperature. The resulting solution was quenched with aqueous NH_4Cl solution and the mixture was extracted with EtOAc. The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The mixture was filtrated and concentrated under reduced pressure. The residue was purified by a silica gel chromatography (hexane/EtOAc = 4/1) to give (*R*)-**5a** as a yellow solid (108 mg, 0.244 mmol, 80%). ^{1}H NMR ($CDCl_3$): δ 1.67 (s, 3H), 2.91-3.07 (m, 2H), 4.36 (br, 1H), 5.00 (br, 1H), 5.22 (br, 1H), 6.16 (br, 1H), 7.36-7.44 (m, 10H), 9.43 (s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.3 (s), 34.7 (d, J_{PC} = 20.7 Hz), 80.5 (s), 80.9 (s), 83.8 (s), 87.2 (s), 103.3 (s), 115.6 (d, J_{PC} = 11.4 Hz), 128.3 (d, J_{PC} = 9.3 Hz), 128.4 (d, J_{PC} = 8.2 Hz), 129.8 (s), 130.1 (s), 131.5 (d, J_{PC} = 9.3 Hz), 131.8 (d, J_{PC} = 10.4 Hz), 136.9 (d, J_{PC} = 42.5 Hz), 137.5 (d, J_{PC} = 43.6 Hz), 138.8 (s), 189.7 (s), 225.1 (d, J_{PC} = 21.8 Hz), 226.3 (d, J_{PC} = 20.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 103.3 (s). ES-HRMS Calcd for $C_{24}H_{20}MnO_3P$: 442.0531. Found: 442.0538. $[\alpha]_D^{12}$ +344 (*c* 1.01 $CHCl_3$ for the sample of >99.9% ee).

(*S*)-(+)-[(η^5-1-(3-Diphenylphosphino-2-methylpropenyl)-cyclopentadienyl-2-vinyl-*P*)]manganese(I) Dicarbonyl (6a). To a solution of $MePPh_3$·Br (106 mg, 0.297 mmol) in THF (6 mL) was added ^{n}BuLi (1.6 M in hexane, 0.19 mL, 0.30 mmol) dropwise at 0 °C, then the mixture was stirred for 20 min at this temperature. To this was added an THF (4 mL) solution of (*R*)-(+)-**5a** (110 mg, 0.249 mmol) via cannula, and the mixture was warmed to room temperature. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/EtOAc = 4/1) to give (*S*)-**6a** as yellow oil (85 mg, 0.191 mmol, 77%). ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 3H), 2.89-3.00 (m, 2H), 4.02 (br, 1H), 4.80 (d, *J* = 2.4 Hz, 1H), 4.93 (br, 1H), 5.09 (d, *J* = 11.2 Hz, 1H), 5.43 (d, *J* = 17.6 Hz, 1H), 5.98 (br, 1H), 6.09 (dd, *J* = 17.6 and 11.2 Hz, 1H), 7.31-7.36 (m, 6H), 7.38-7.41 (m, 2H), 7.45-7.49 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.1 (d, J_{PC} = 4.6 Hz), 35.5 (d, J_{PC} = 19.1 Hz), 76.2 (d, J_{PC} = 1.1 Hz), 76.5 (s), 82.2 (d, J_{PC} = 1.5 Hz), 92.9 (s), 99.8 (d, J_{PC} = 2.1 Hz), 112.8 (s), 116.9 (d, J_{PC} = 11.9 Hz), 128.0 (d, J_{PC} = 9.3 Hz), 128.1 (d, J_{PC} = 9.2 Hz), 128.45 (s), 128.46 (d, J_{PC} = 3.6 Hz), 129.8 (s), 131.7 (d, J_{PC} = 9.9 Hz), 131.9 (d, J_{PC} = 10.5 Hz), 137.6(s), 137.8 (d, J_{PC} = 41.5 Hz), 148.2 (d, J_{PC} = 40.4 Hz), 230.6 (d, J_{PC} = 19.7 Hz), 231.0 (d, J_{PC} = 18.2 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 107.9 (s). ES-HRMS Calcd for $C_{25}H_{22}MnO_2P$: 440.0738. Found: 440.0736. $[\alpha]_D^{24}$ +535 (*c* 0.95, $CHCl_3$ for the sample of >99.9% ee).

ASSOCIATED CONTENT

Supporting Information. NMR spectra (^{1}H, ^{13}C and ^{31}P) and for all the new compounds, chiral HPLC chromatograms, and crystallographic data for (*R*)-(−)-**2a** (in CIF format).

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Notes

The authors declare no competing financial interest.

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